Absorption Spectra of the Vapors of Twelve Alcohols and of Nitric Acid in the Region of the O—H Harmonic Band at λ9500*

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(Received August 3, 1936)

The absorption spectra of the vapors of twelve alcohols and of nitric acid have been investigated by photographic methods in the region λλ9450–9850. In each case a strong harmonic band of the O—H vibration was found. In the primary alcohols and in *o*-chlor phenol the O—H vibration was found to split into two components, a possible explanation for which is briefly discussed. In the bands of certain other substances a considerable complexity of structure was observed which is attributed either to a free rotation or a torsional vibration of the hydroxyl hydrogen with respect to the remainder of the molecule. Systematic shifts in the frequency of the O—H vibration with changes in the structure of the alcohol molecule were found.

INTRODUCTION

THE authors have recently become interested in the study of the spectra of molecules in which there is the possibility of either a free rotation of two parts of the molecule with respect to each other, about a certain bond, or at least of a restrained rotation or torsional vibration. The theory of spectra of this type is in a very undeveloped state and its extension to other than the simplest cases appears to be extremely difficult. Consequently the best method of attack at present appears to be the comparative study of a number of similar substances in an attempt to find empirical relationships and if possible to develop a qualitative semi-classical picture which will account for the observed facts.

Substances containing the hydroxyl radical are especially convenient for study in the photographic infrared since the O—H harmonic bands appear with great intensity and the vibration which gives rise to them is nondegenerate in the ordinary sense though, as will be seen, it occasionally splits into two components. In a recent paper[1] we have described two bands of methyl alcohol which have a complex structure evidently due to the type of degree of freedom above mentioned. The present paper extends the investigation to eleven other alcohols and to nitric acid, all of which were studied in the vapor state in the region λλ9450–9850, in which bands corresponding to the transition 0→3 in the O—H vibration are found.

The next lower harmonic of the O—H vibration in certain of these substances, when in dilute solution in carbon tetrachloride, has been examined by Wulf and Liddel.[2] Our results are in agreement with those of these workers insofar as a comparison may be made. However, since we have worked with the substances in the vapor state and with high dispersion we have uncovered considerable complexity of structure which is wiped out in the liquid condition.

EXPERIMENTAL

The experimental procedure was essentially the same as that used in the investigation of methyl alcohol,[1] except that the ten-foot absorption tube of glass was used in each case. Exploratory photographs were taken with a glass spectrograph which has a dispersion of 70A per mm at λ9000, to locate the absorption region in each case. A more intensive examination was then made with the grating spectrograph which has a dispersion of about 2.5A per mm. The final measurements were made, in most cases, on microphotometer curves using water vapor lines as references. Because of the weakness of water lines at λ9800 the *B* band of *o*-chlor phenol and the band of nitric acid were measured with reference to iron lines in the second and third orders.

The alcohols investigated were of the highest purity which we could conveniently obtain. They were first dried with anhydrous sodium sulfate

* This investigation is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

[1] Badger and Bauer, J. Chem. Phys. **4**, 469 (1936).

[2] Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).

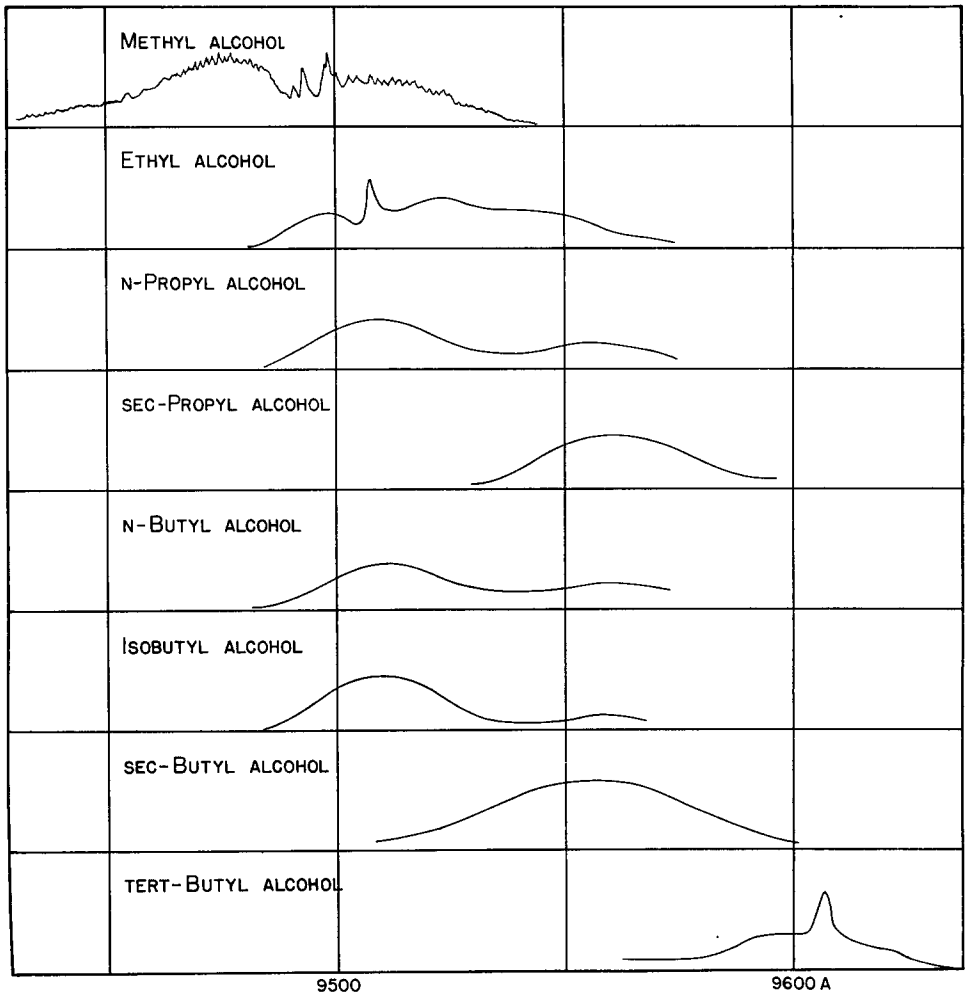

FIG. 1. Microphotometer curves of the O—H harmonic bands in the vapors of eight aliphatic alcohols in the λ9500 region.

or sometimes with metallic sodium, and were then fractionated in a four-foot bead-filled column when a sufficient quantity of the material was available. In the case of *o*-chlor phenol we took particular care that no appreciable amount of phenol was present as impurity. From comparisons of the freezing and boiling points of our substance with those of a sample to which a trace of phenol had been added we estimate that the maximum amount of this impurity which could have been present was less than 2 percent.

The nitric acid was prepared by the action of concentrated sulfuric acid on potassium nitrate. A rather pure product was apparently obtained but after a short time in the heated absorption tube some decomposition took place and the tube became opaque except to the red and longer wave-lengths. The oxides of nitrogen produced by the decomposition absorb extremely weakly in the region in which we were interested and did not interfere in any way.

The spectra of all the substances reported on were obtained at pressures between one-half and one atmosphere.

The results of the investigation are set forth in Figs. 1 and 2, in which are shown microphotometer tracings of the plates taken with high dispersion. In Fig. 2 the *A* band of *o*-chlor phenol has been reproduced on a considerably enlarged vertical scale to show its shape more clearly. We estimate this band to have between one-seventh and one-eighth the intensity of the

TABLE I. *Absorption maxima in the O—H harmonic bands of the vapors of eight aliphatic alcohols in the region λ9500.*

Type of alcohol	Example	Formula	Absorption maximum λ (A)	Absorption maximum ν (cm⁻¹)
—	Methyl	CH_3OH	9493.1 (Q?)	10531.1
primary	Ethyl	CH_3CH_2OH	A 9499	10524
			A 9507.8 (Q)	10514.8
			A 9524	10497
			B (9547)	(10472)
	n-Propyl	$C_2H_5CH_2OH$	A 9510	10512
			B 9557	10461
	n-Butyl	$C_2H_5CH_2CH_2OH$	A 9512	10510
			B 9560	10457
	iso-Butyl	$(CH_3)_2CHCH_2OH$	A 9510	10512
			B 9559	10458
secondary	*sec*-Propyl	$(CH_3)_2CHOH$	9561	10456
	sec-Butyl	$C_2H_5CH(OH)CH_3$	9557	10461
tertiary	*tert*-Butyl	$(CH_3)_3COH$	9607.3	10405 9

TABLE II. *Absorption maxima in the O—H harmonic bands of the vapors of some other substances.*

Substance	Formula	Absorption maximum λ (A)	Absorption maximum ν (cm⁻¹)
Allyl alcohol	$H_2C\ CHCH_2OH$	9566	10451
Ethylene glycol	$HOCH_2CH_2OH$	9547 ?	10471
		9610 ?	10403
Phenol	C_6H_5OH	9553 4	10464 6
		9559.5	10457.9
		9565.0 (Q?)	10451.8
		9569.6	10446 8
o-Chlor phenol	C_6H_4ClOH	A 9573	10443
		B 9812	10189
Nitric acid	$HONO_2$	9819	10183
		9826	10174
		9829.9 (Q)	10170.2
		9838.9	10160.9
		9846.1	10153.5

B band at 160°C. The microphotometer curves have been corrected for the superposed water spectrum which could not be eliminated entirely except in the longer wave-length portion of the region investigated. This correction may be a trifle uncertain in the case of methyl alcohol, the only substance which showed any resolvable rotational structure of the ordinary sort, and possibly also in phenol, though it cannot be greatly in error. In all other cases it could be made very easily owing to the broad, continuous character of the bands and the extreme sharpness of the water lines.

Microphotometer curves are not given for allyl alcohol and ethylene glycol. Our plates of the former substance are not entirely satisfactory though it seems quite clear that there is but one absorption region which is similar to that of the secondary alcohols. Ethylene glycol absorbs very weakly indeed and we were unable to get satisfactory plates under high dispersion. The measurements given were made on a low dispersion plate and the accuracy is not great. There appear to be two maxima of absorption though this is not quite certain.

DISCUSSION

The aliphatic alcohols

As will be seen in Fig. 1, the spectra of the four primary alcohols studied which contain the group CCH_2OH, are very similar. They all possess a strong absorption region around λ9510, and another around λ9560 which is much weaker

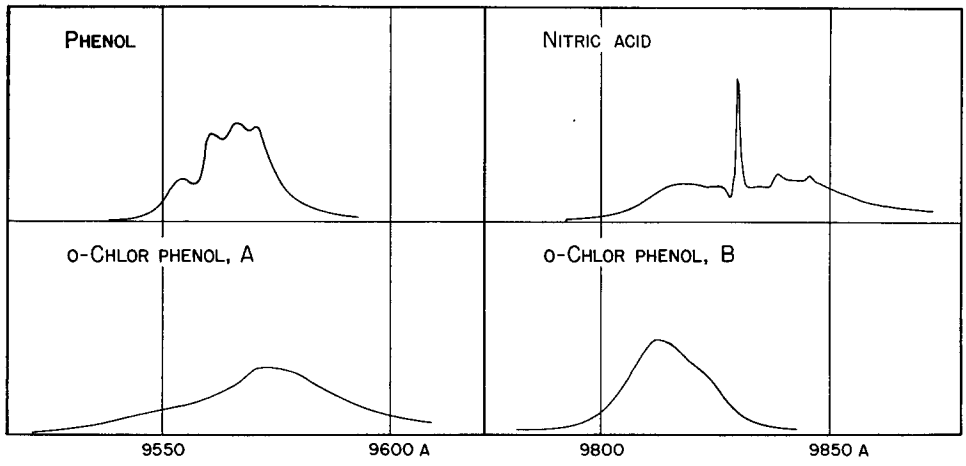

FIG. 2. Microphotometer curves of the O—H harmonic bands in the vapors of phenol, *o*-chlor phenol and nitric acid. The vertical scale of the *A* band of *o*-chlor phenol is enlarged about five times relative to that of the *B* band.

but quite definitely present. Ethyl alcohol shows some special features for which a possible explanation is suggested below. The spectra of the two secondary alcohols examined are practically identical. In each case there is a single absorption region at about λ9560. Unfortunately we have only one example of a tertiary alcohol, which is in some respects a special case. We hope later to study the amyl alcohols but this will necessitate some changes in our experimental arrangements. It is possible that some of the amyl alcohols will show anomalies, which indeed seems to be indicated in *sec*-isoamyl alcohol by the work of Wulf and Liddel.[2]

It is interesting to note that as each of the hydrogen atoms of the methyl group in methyl alcohol is replaced by an aliphatic radical the major absorption region shifts by a more or less definite amount. Due to the complex structure of the methyl alcohol band and the uncertainty as to what we shall regard as its center, it is difficult to say what this shift is as the first hydrogen is replaced, but in the second and third steps it is practically constant and amounts to about 54 cm^{-1}. This shift cannot be entirely or even largely a mass effect due to the similarity of the spectra of all the primary alcohols, and likewise of the secondary alcohols. It is impossible to say what shift should be expected from the mass effect alone since a normal coordinate treatment of the alcohols would be practically impossible at present. In any case it appears reasonable to us to attribute the effect largely to a change in the strength of binding which is indicated by the differences in reactivity, heats of combustion, etc., of the primary, secondary and tertiary alcohols.

It is interesting that the absorption band of allyl alcohol lies very close to those of the secondary alcohols. Since the structure of this substance appears to be well established by chemical evidence it would appear that there must be a rather large interaction between the O—H bond and the double bond.

The weakness of the absorption found in ethylene glycol is possibly due to chelation or association.

Phenol and *o*-chlor phenol

The O—H frequency in phenol lies between those of the secondary and tertiary alcohols, which is about what one would expect. The structure of the band observed is rather complex and resembles in some respects those found for methyl alcohol, though it is more compressed. When a chlorine atom is introduced into phenol in the *ortho* position the O—H band splits into two components, the stronger of which is shifted about 260 cm^{-1} and the weaker about 10 cm^{-1} to the low frequency side of the phenol band. These two bands of *o*-chlor phenol have a similar appearance. Much of the complexity of structure found in phenol has been lost though there is some indication that each of the component bands may consist of two branches of unequal intensity.

An explanation of the splitting of the O—H frequency in *o*-chlor phenol has been given by Pauling[3] who believes that the two potential minima which would be encountered if the hydroxyl hydrogen were to rotate are sufficiently deep to prevent free rotation and to keep the molecule in either of two possible configurations in which the O—H vibration has somewhat different frequencies.

Nitric acid

Our work on the vapor definitely establishes the presence of an hydroxyl group in the undissociated nitric acid molecule. In pure liquid nitric acid the O—H frequency should certainly be very weak due to the possibility of hydrogen bond formation. In one case it has been reported as present,[4] though somewhat doubtful, in the Raman spectrum of the liquid, but other workers have failed to find it. However, six other Raman lines[4, 5] appear to be well established as characteristic of the undissociated molecule, namely those with frequency shifts of approximately: 607, 667, 916, 1292, 1665 and 1687 cm^{-1}. In

TABLE III. *Provisional correlation of the frequencies of the nitrate ion with those of the undissociated nitric acid molecule.*

Nitrate ion	Nitric acid molecule
1071 (valence vibration, non-degenerate)	1292
1389 (degenerate)	1665 1687
726 (degenerate)	607 667
830 (bending out of plane)	916

[3] L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).
[4] Dadieu and Kohlrausch, Naturwiss. **19**, 690 (1931).
[5] Aderhold and Weiss, Zeits. f. Physik **88**, 83 (1934).

comparing these with the frequencies of the nitrate ion as found in crystals[6] and in aqueous solutions of the nitrates[7] and of nitric acid[5] it appears that there is a certain correlation. However, there is a considerable frequency shift and the two degenerate frequencies of the nitrate ion appear to split in nitric acid, showing the absence of a threefold axis.

In Table III is given a provisional assignment of frequencies in relation to those of the nitrate ion.

This leaves two vibrations still to be assigned, both of which are bending motions which chiefly involve the hydrogen atom. Owing to association in the liquid, which must greatly affect their character, they will have to be investigated in the vapor condition or in dilute solutions of the acid in some nonionizing solvent. One of these vibrations may be of moderately high frequency, the other may border on free rotation and we believe it is responsible for the complex structure of the band at λ9830 which we have investigated.

Methyl alcohol, *tert*-butyl alcohol, phenol and nitric acid

The spectra of these substances all possess a relatively great complexity and have certain features in common, in particular the presence of one or more Q branches. It appears to us that in these cases we have a closer approach to free rotation of the hydroxyl hydrogen than in the other substances which we have studied, which may be responsible for the particular type of structure. A further important similarity is that each of the molecules, exclusive of the hydroxyl hydrogen, has an axis of symmetry about which this atom will rotate in case it is free to do so. In methyl alcohol and *tert*-butyl alcohol this axis is threefold, in the other two cases it is twofold.

The two absorption regions of the primary alcohols

It is possible that the two absorption regions of the primary alcohols may have an explanation similar to that applicable to *o*-chlor phenol. Pauling's interpretation of this last case has been mentioned. It is certainly very suggestive although it is not clear to us that it is complete,

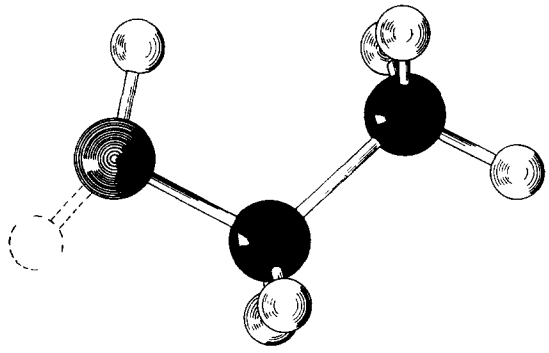

FIG. 3. Model of the ethyl alcohol molecule showing two orientations of the hydroxyl hydrogen which may correspond to minima of potential energy.

especially in view of the unexpected complexity of the phenol band. However, it appears that in ethyl alcohol there are two orientations of the hydroxyl hydrogen which may well correspond to potential minima, as shown in Fig. 3. In one of these the environment of this atom will be similar to that in methyl alcohol, in the other it will be considerably different. Furthermore, in the former orientation the change in electric moment will have a large component in the direction of the axis of least moment of inertia, in the latter it will be nearly perpendicular to this axis, which may account for the presence or absence of a Q branch in the two absorption regions, respectively.

In the higher primary alcohols the hydrocarbon chain is much more likely to be found in an extended than in a coiled condition. As evidence for this statement we may mention the well-known measurements on the thickness of surface films of polar molecules. This being the case the situation with regard to the hydroxyl hydrogen will be very similar in most primary alcohols.

In the secondary alcohols it is rather more difficult to see what configurations may correspond to potential minima. Since the observed spectrum is a rather broad band with a single maximum and no observable structure it may be that the environment of the hydroxyl hydrogen is not very different in the various positions it may occupy.

The authors plan to extend the type of investigation here described to the study of a series of amines and similar compounds, including hydroxylamine and hydrazine.

[6] A. C. Menzies, Proc. Roy. Soc. **A134**, 265 (1931).
[7] P. Grassman, Zeits. f. Physik **77**, 616 (1932).